

(B)

REF ID:  
A628

AD

CHEMICAL SYSTEMS LABORATORY TECHNICAL REPORT

ARCSL-TR-80060

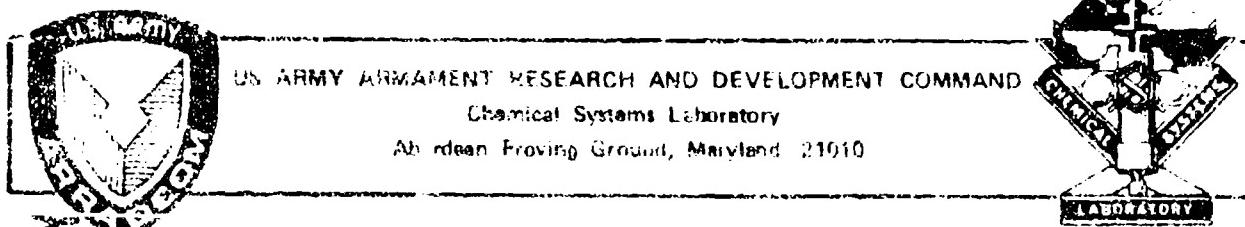
AN IMPROVED THERMODYNAMIC MODEL FOR PHOSPHORUS SMOKE

by

Glenn O. Rubel

Research Division

April 1981



Approved for public release; distribution unlimited.

FILE COPY

FILE

ED

**BEST**

**AVAILABLE**

**COPY**

#### **Disclaimer**

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

#### **Disposition**

Destroy this report when it is no longer needed. Do not return it to the originator.

~~UNCLASSIFIED~~

**SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)**

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-80060	2. GOVT ACCESSION NO. <i>AD-A100 296</i>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) AN IMPROVED THERMODYNAMIC MODEL FOR PHOSPHORUS SMOKE	5. TYPE OF REPORT & PERIOD COVERED Technical Report January-November 1979	
7. AUTHOR(s) Glenn O. Rubel	6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander/Director, Chemical Systems Laboratory ATTN: DRDAR-CLB-PS Aberdeen Proving Ground, Maryland 21010	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS IT161102A71A Scientific Area 5	
11. CONTROLLING OFFICE NAME AND ADDRESS Commander/Director, Chemical Systems Laboratory ATTN: DRDAR-CLJ-R Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE April 1981	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES 29	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.	15. SECURITY CLASS. (of this report)  UNCLASSIFIED	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)	18. DECLASSIFICATION/DOWNGRADING SCHEDULE NA	
19. SUPPLEMENTARY NOTES		
20. KEY WORDS (Continue on reverse side if necessary and identify by block number) Yield factor Acid fraction Water activity	Orthophosphoric acid Condensed phosphoric acid	
21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Orthophosphoric acid is commonly employed to represent the solution thermodynamics of phosphorus smoke droplets. However, transmission measurements in the 8- to 12- $\mu$ m region demonstrate significant disparities between phosphorus smoke and comparable orthophosphoric acid mists. Since the transmission characteristics in the 8- to 12- $\mu$ m region are primarily due to absorption by specific molecular species, it may be concluded the acid species of phosphorus smoke is not solely orthophosphoric acid.  It is the intent of this study to delineate the expected range of error resulting from the use of an orthophosphoric acid thermodynamic model for the prediction of the physico-chemical (see continuation on reverse side)		

**UNCLASSIFIED**

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

**20. ABSTRACT. Contd**

properties of a phosphorus smoke under tactical conditions. Results show the orthophosphoric acid model underestimates phosphorus smoke acid fractions by as much as 25% for relative humidities less than 90%.

The water activity of an arbitrary mixture of condensed phosphoric acids is derived from the orthophosphoric acid water activity model through a solute number reduction scheme. Asserting the acid mixture is 75% pyrophosphoric acid and 25% orthophosphoric acid, phosphorus smoke data are accurately predicted by mixture model calculations.

Accommodation For	
Medical	<input checked="" type="checkbox"/>
Administrative	<input type="checkbox"/>
Logistics	<input type="checkbox"/>
Scientific	<input type="checkbox"/>
Other	
Classification Codes	
Initial Classification	
A	

## SUMMARY

Orthophosphoric acid is commonly resorted to when physical property data are required to model phosphorus smoke. It has been shown previously that optical constants of orthophosphoric acid solutions provide reasonably accurate approximations to the extinction properties of phosphorus smoke in the visible, near infrared (IR), and 3- to 5- $\mu\text{m}$  IR region, but not in the 8- to 12- $\mu\text{m}$  region. Furthermore, studies on the high-temperature reaction between phosphorus pentoxide and water vapor, a precursor reaction to the formation of a phosphorus smoke, indicates the chemical composition of the smoke droplets is a mixture of condensed phosphoric acids. From these results, it is clear that phosphorus smoke is not composed entirely of orthophosphoric acid.

It is the intent of this study to delineate the expected range of errors resulting from the employment of an orthophosphoric acid thermodynamic model for the prediction of the equilibrium properties of a phosphorus smoke under tactical conditions. Subsequently, the thermodynamic properties of the solution droplets comprising a phosphorus smoke are formulated by accounting for the condensed nature of the phosphoric acids. By considering the condensed phosphoric acids as a homologous series, the solution thermodynamics of the condensed phosphoric acids is approximated from the orthophosphoric acid water activity data by applying a solute number reduction scheme.

Asserting the acid mixture is a combination of pyrophosphoric acid and orthophosphoric acid, a mixture model is proposed for the representation of a phosphorus smoke. Comparison of mixture model data and experimental data indicates the mixture model predicts the acid concentrations and yield factors of a phosphorus smoke within 5%. This represents a significant improvement over the 25% errors resulting from the orthophosphoric acid model predictions.

PREFACE

The work described in this report was authorized under Project 1T161102A71A, C/B Defense and General Investigations; Scientific Area 5, Aerosol/Obscuration Science. This work was conducted from January to November 1979. The background data are contained in notebook 9990.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander/Director, Chemical Systems Laboratory, ATTN: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010; however, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for United States Government purposes.

## CONTENTS

	Page
1 INTRODUCTION .....	9
2 THERMODYNAMIC PROPERTIES OF ORTHOPHOSPHORIC ACID DROPLETS.....	9
3 REFORMULATION OF PHOSPHORUS SMOKE THERMODYNAMIC PROPERTIES.....	14
3.1 Solution Thermodynamics of Condensed Phosphoric Acids .....	15
3.2 Equivalent $H_3PO_4$ Phosphorus Smoke Acid Concentration .....	17
3.3 Real Phosphorus Smoke Acid Concentration .....	19
3.4 Yield Factor of a Phosphorus Smoke .....	21
4 CONCLUSIONS .....	22
LITERATURE CITED .....	23
GLOSSARY .....	25
DISTRIBUTION LIST .....	27

## LIST OF FIGURES

### Figure

1 Acid Concentrations of a Phosphorus Smoke Versus Relative Humidity .....	12
2 Yield Factors of a Phosphorus Smoke Versus Relative Humidity.....	14
3 Water Activity of Various Condensed Phosphoric Acid Solutions in a Function of $H_3PO_4$ Association .....	16
4 Equivalent $H_3PO_4$ Acid Concentation of a Phosphorus Smoke Versus Degree of Acid Association .....	18
5 Percent Deviation between Equivalent $H_3PO_4$ and Real Acid Concentration as a Function of Acid Association.....	20

## TABLE

Dependence of Kelvin Effect on Droplet Diameter for Sized Representative of a Phosphorus Smoke.....	10
---	----

## AN IMPROVED THERMODYNAMIC MODEL FOR PHOSPHORUS SMOKE

### 1. INTRODUCTION

To accurately predict the condensational growth of a phosphorus smoke and its attendant obscuration efficiency, detailed knowledge of the solution thermodynamics of the acid droplets is required. Previous attempts to model the thermodynamic properties of a phosphorus smoke<sup>1</sup> have been based on the assumption that the generic acid of the solution droplets is orthophosphoric acid ( $H_3PO_4$ ). However, recent transmission measurements by Milham *et al.*<sup>2</sup> have indicated the optical properties of a phosphorus smoke are distinctly different from these of a comparable  $H_3PO_4$  mist. These findings coupled with the high-temperature phosphorus pentoxide ( $P_4O_{10}$ ) hydration studies by Kapishev<sup>3</sup> clearly indicate that a phosphorus smoke is not composed entirely of  $H_3PO_4$ .

It is the purpose of this study to address the expected range of errors resulting from the representation of a phosphorus smoke by a thermodynamic model that is based on the solution properties of  $H_3PO_4$ . Having demonstrated the inadequacies of the previous model, a more realistic thermodynamic model is formulated by accounting for the condensed nature of the droplet phosphoric acids. Based on the high temperature  $P_4O_{10}$  hydration studies by Kapishev, it is postulated the acid components of a phosphorus smoke are 75% pyrophosphoric acid and 25%  $H_3PO_4$  by weight. The solution thermodynamics of an arbitrary mixture of condensed phosphoric acids is established from the  $H_3PO_4$  water activity data through a solute number reduction scheme. Comparison of mixture model synthetic data and  $H_3PO_4$  model predictions with experimental data taken from a phosphorus smoke shows that, although errors of 25% are associated with the  $H_3PO_4$  model, maximum errors of only 5% result from the mixture model predictions. The theoretical development of a thermodynamic model for the condensed phosphoric acids is believed to be a more robust representation of phosphorus smokes than previous empirical attempts.

### 2. THERMODYNAMIC PROPERTIES OF ORTHOPHOSPHORIC ACID DROPLETS

The acid droplets are proposed to be mixtures of volatile water and nonvolatile acids. In general, the water partial pressure over the droplet surface is a function of the droplet diameter and droplet acid concentration. At constant temperature T and total pressure P, the droplet saturation ratio S is found by minimizing the solution droplet Gibbs free energy. The droplet saturation ratio, the degree of water saturation at the droplet surface, is given by

$$\ln S = -\frac{4\sigma v}{RTd} + \ln a_1 \quad (i)$$

The first term on the right-hand side is referred to as the Kelvin effect, a vapor pressure elevation effect. The Kelvin effect causes very small droplets to have extremely high vapor pressures, whereas the larger droplets are affected to only a small extent. The table illustrates the increase in vapor pressure over phosphoric acid droplets due to its increasing curvature. It is evident that, for droplets with diameter greater than 0.3  $\mu\text{m}$ , the Kelvin effect represents less than a 1% elevation in the droplet vapor pressure.

Table. Dependence of Kelvin Effect on Droplet Diameter  
for Sizes Representative of a Phosphorus Smoke

Exp $4\sigma v_1 / RTd$	d
	$\mu\text{m}$
1.23	0.01
1.02	0.10
1.01	0.30
1.00	1.00

Cascade impactor measurements by Gillespie and Johnstone<sup>4</sup> show that only those droplets with diameter greater than 0.3  $\mu\text{m}$  contribute significantly (>99%) to the phosphorus smoke mass distribution. Consequently, thermodynamic properties of the non-Kelvin phosphoric acid droplets are completely specified by the relation

$$S = a_1 \quad (2)$$

The water activity  $a_1$  of the acid solutions is defined as the ratio of the water pressure over the acid solution to the saturation water vapor pressure at the solution temperature. The nonvolatile acid depresses the water vapor pressure and the droplet saturation ratio will be less than unity.

From water vapor pressure data over a discrete set of  $\text{H}_3\text{PO}_4$  solutions as given by Mellor,<sup>5</sup> the water activity of  $\text{H}_3\text{PO}_4$  solutions can be analytically related to the water mole fraction. Toward the aim of finding a continuous analytic relationship, a nonlinear regression analysis is applied to the water activity data. Within a 2% error, the water activity of  $\text{H}_3\text{PO}_4$  solutions can be represented by the multivalued function

$$\begin{aligned} a_1 &= -7.812x_1^3 + 18.828x_1^2 - 12.703x_1 + 2.711 & 0.10 < a_1 < 0.75 \\ a_1 &= -6.343x_1^2 + 13.649x_1 - 6.308 & 0.75 < a_1 < 0.99 \end{aligned} \quad (3)$$

It has been shown previously by Rubel<sup>1</sup> that the acid nuclei produced by the combustion of elemental phosphorus condensationally grow to a stable equilibrium within seconds of formation. These calculations have been experimentally supported by the acid concentration-residence time measurements of Gillespie and Johnstone.<sup>4</sup> Stable equilibrium for a solution droplet is defined as the condition where the droplet saturation ratio equals the environmental relative humidity. Therefore, the acid droplets have achieved diffusional equilibrium under tactical conditions and

$$S = \Psi$$

By inverting equation 4, the water mole fraction can be defined in terms of the relative humidity  $\Psi$  as

$$\begin{aligned} x_1 &= 0.632 \cos [\cos^{-1} (1.175 - 1.928\Psi)/3 + 240] + 0.803 & 0.11 < \Psi < 0.75 \\ x_1 &= \frac{2.152 - (0.655 - 0.632\Psi)^{1/2}}{2} & 0.75 < \Psi < 0.99 \end{aligned} \quad (4)$$

From the defining relationship between acid fraction F and water mole fraction  $x_1$

$$x_1 = \frac{1.000 - F}{1.00 - 0.816F} \quad (5)$$

the acid fraction of an  $H_3PO_4$  droplet can be given as

$$F = \frac{0.197 - 0.632C}{0.345 - 0.516C} \quad 0.11 < \Psi < 0.75$$

where

$$C = \cos \frac{[\cos^{-1} (1.219 - 2.00\Psi) + 240]}{3} \quad (6)$$

and

$$F = \frac{-0.076 + 0.500 (0.655 - 0.632\Psi)^{1/2}}{0.122 + 0.408 (0.655 - 0.632\Psi)^{1/2}} \quad 0.75 < \Psi < 0.99$$

It is noteworthy that the droplet acid concentration  $F$  is independent of the droplet diameter and is solely a function of relative humidity. As a consequence, all acid droplets are characterized by the same acid concentration at a given relative humidity.

Anderson\* measured the acid concentration of phosphorus smoke liquid from 20% to 90% relative humidity. The measurement involved titrating the liquid sample against a standard 0.01 N NaOH solution. The  $H_3PO_4$  molecule strongly dissociates one hydrogen ion allowing for a substitution by the sodium ion. Since  $H_3PO_4$  is primarily monoprotic, each mole of NaOH dissolved is equated to a mole of  $H_3PO_4$ . From the total mass of sample and the moles of  $H_3PO_4$  present, the  $H_3PO_4$  concentration is determined.

Figure 1 shows the differences between measured acid fractions and those values predicted by the  $H_3PO_4$  model. The ortho model consistently underestimates the acid concentrations over the relative humidity range from 20% to 90%. Errors vary from 14% at 25% relative humidity to as high as 25% at 90% relative humidity. This would suggest the ortho model overestimates the water absorbing characteristics of the acid droplets. Since the specific solution acid controls the degree of condensational growth, the disparities indicate the generic acid is not  $H_3PO_4$ .

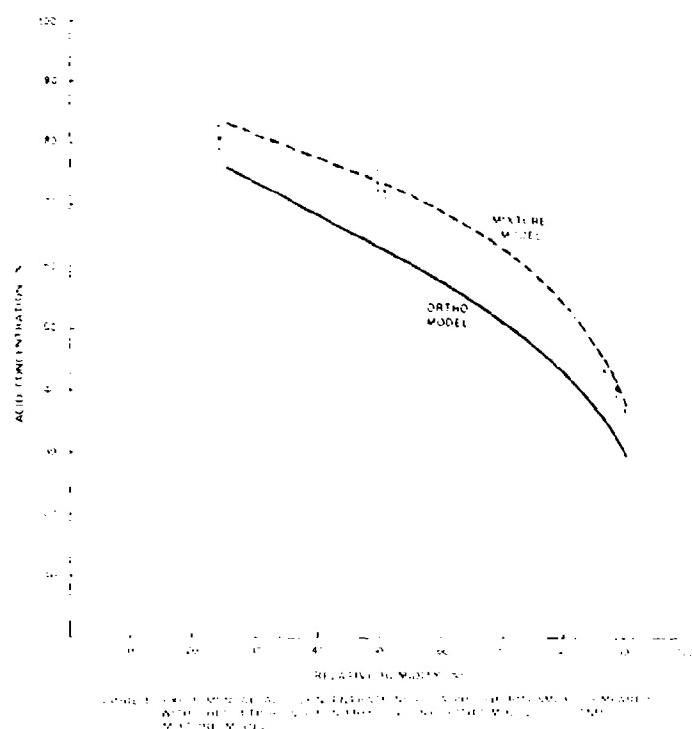


Figure 1. Acid Concentrations of a Phosphorus Smoke Versus Relative Humidity

\* Anderson, D. H. Chemical Systems Laboratory, Research Division, Aberdeen Proving Ground, Maryland. Private communication. 1978.

A further indication of the inadequacies of the ortho model is the significant differences between measured and predicted yield factors. The yield factor (y.f.) is defined as the ratio of the final aerosol mass to the mass of starting smoke generating material. If the smoke material is pure phosphorus and each phosphorus atom in the starting material is aerosolized, then the phosphorus smoke yield factor is<sup>1</sup>

$$y.f. = \frac{M(H_3PO_4)}{M(P) * F} \quad (7)$$

where  $M(H_3PO_4)$  is the molecular weight of the  $H_3PO_4$  molecule and  $M(P)$  is the mass of the phosphorus atom.

Equation 9 illustrates the mass increase of a starting phosphorus atom as it is chemically converted to  $H_3PO_4$  which then experiences water absorption according to its thermodynamic properties. To predict the mass of phosphorus smoke generated by a pure phosphorus starting material, the initial mass is scaled upward by the appropriate relative humidity dependent yield factor. In general, all of the starting phosphorus is not aerosolized due to perhaps burning efficiencies associated with the design of the starting material. The phosphorus aerosolization parameter  $\zeta$ , which is normally less than unity, is defined as the ratio of phosphorus in the aerosol state to the phosphorus in the starting material. Furthermore, a particular smoke material may be composed of phosphorus and nonphosphorus material. Consequently, the realized yield factor is expressed in terms of the material yield factor as

$$y.f. (\text{realized}) = n * \zeta * y.f. (\text{material}) \quad (8)$$

where  $n$  is the percent mass of phosphorus in the starting material. Tarneve<sup>6</sup> measured the material yield factor of a phosphorus smoke for relative humidities between 40% and 70% relative humidity. Figure 2 depicts the disparities between measured and ortho model predicted yield factors. The ortho model overestimates the measured yield factors by as much as 25%. The overestimation of mass is a combination of generic acid and attendant solution thermodynamics misrepresentation.

Since the disparities are significant, it may be concluded that the  $H_3PO_4$  model cannot satisfactorily describe the thermodynamic properties of a phosphorus smoke. In fact, the failure of the ortho model is not totally unexpected if one considers the high temperature hydration of  $P_4O_{10}$ , a precursory reaction to the formation of a phosphorus smoke. Although it is commonly assumed that the  $P_4O_{10}$  hydration product is  $H_3PO_4$ , Kapishev<sup>3</sup> has found that, for temperatures about 200°C, the hydration reaction results in a mixture of condensed phosphoric acids. Only after days will these condensed acids revert to  $H_3PO_4$ .<sup>5</sup>

Therefore, to accurately model the condensational growth of a phosphorus smoke, thermodynamic data are required on the solution thermodynamics of the condensed phosphoric acids. Unfortunately, the thermodynamic data on the condensed phosphoric acids are sparse. However, the water activity of the condensed phosphoric acids may be heuristically formulated by invoking key assumptions.

### 3. REFORMULATION OF PHOSPHORUS SMOKE THERMODYNAMIC PROPERTIES

The combustion of elemental phosphorus establishes a severe supersaturation of  $P_4O_{10}$  vapor. The nucleation of the oxide is most probably governed by the sublimation characteristics of the  $P_4O_{10}$  having a sublimation temperature of around  $250^\circ C$ .<sup>5</sup> Once nucleated, the oxide chemisorbs water vapor and converts to a phosphoric acid. Kapishev<sup>3</sup> experimentally analyzed the high-temperature hydration reaction between  $P_4O_{10}$  and water vapor. Employing chromatographic methods, the researchers concluded that the resultant liquid was a mixture of condensed phosphoric acids whose percent composition was temperature dependent. For chemisorption at  $20^\circ C$  the percent weight composition of the mixture was determined to be 25%  $H_3PO_4$  and 75% pyrophosphoric acid. This acid composition will represent the hygroscopic solute employed in the following analysis of phosphorus smoke growth.

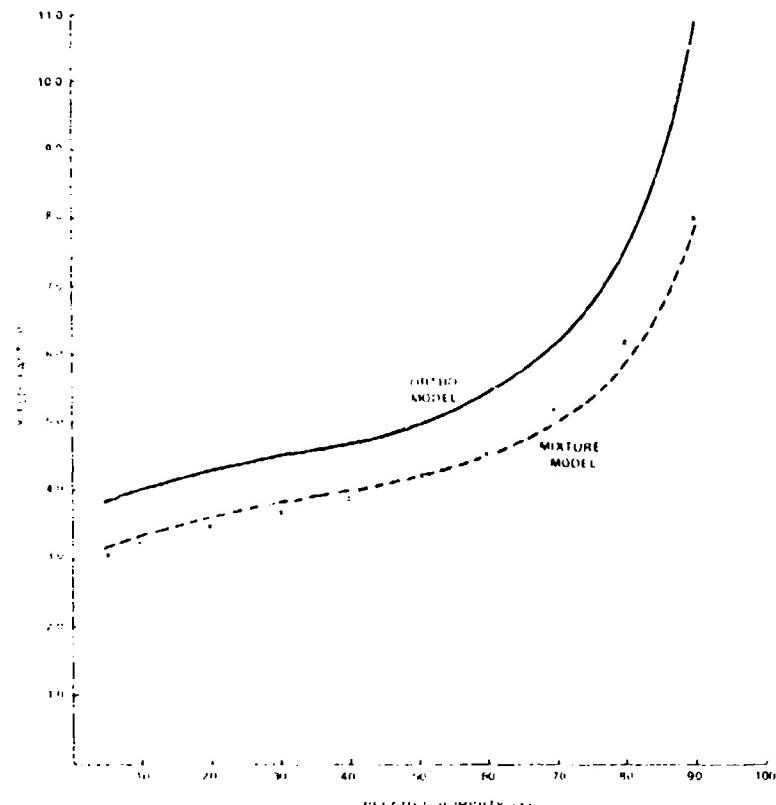


FIGURE 2. EXPERIMENTAL YIELD FACTORS OF A PHOSPHORUS SMOKE COMPARED WITH THEORETICAL VALUES PREDICTED ORTHO MODEL (—) AND MIXTURE MODEL (---).

Figure 2. Yield Factors of a Phosphorus Smoke Versus Relative Humidity

Solution Thermodynamics of Condensed Phosphoric Acids.

The homologous series of condensed phosphoric acids can be represented by the chemical formula<sup>7</sup>



where  $i$  represents the order of phosphoric acid association, i.e.,  $i = 1 + H_3PO_4$  and  $i = 2 \rightarrow H_4P_2O_7$ , orthophosphoric and pyrophosphoric acid, respectively. Therefore, the condensed phosphoric acids can be thought of as physiochemical molecular associations of  $H_3PO_4$  molecules, except for small differences in molecular weight.

The water activity of a solution is a strong decreasing function of the relative number of solute (acid) molecules in solution. Since the associated solution is characterized by a smaller number of solute molecules, the associated solution water activity is greater than the unassociated solution water activity for the same mass of acid.<sup>8</sup> This conclusion was numerically supported by the calculations of Ogsten and Winzer,<sup>9</sup> who considered the effects of associating solutes on the osmotic pressure of a solution. Consequently, for the same mass of acid, the associated solution will absorb a smaller amount of water than the unassociated solution. The associated acid concentration will be correspondingly greater than the unassociated acid concentration. Such a circumstance would explain the disparities depicted figure 1.

The acid mixture solvent mole fraction may be written as

$$x'_1 = \frac{n' H_2O}{n' H_2O + \sum n_i} \quad (10)$$

where  $\sum n_i$  is the number of condensed phosphoric acids resulting from the association of  $\sum n_i H_3PO_4$  molecules. This follows from the hydration process of condensed phosphoric acids where the  $i$ th order condensed phosphoric acid produces  $i$  molecules of  $H_3PO_4$ .<sup>5</sup> The mixture solvent mole fraction can be expressed in terms of the ortho model parameters by the relations

$$n_{H_2O} = n' H_2O \quad \text{and} \quad \frac{\sum n_i}{\sum n_i} = a \quad (11)$$

where the association parameter  $a$  represents the degree of  $H_3PO_4$  molecule association. Substitution of equation 11 into equation 10 gives

$$x'_1 = a / (a + \sum n_i / n_{H_2O}) \quad (12)$$

In general, deviations from Raoult's law result from solute-solvent interactions.<sup>8</sup> Due to a strong hydrogen association,  $H_3PO_4$  appears electronegative in solution. Consequently, high dipole moment water molecules will interact with ionized  $H_2PO_4^-$  molecules. It is asserted that this mode of solvent-solute interaction is the basis for the nonideality of  $H_3PO_4$  solutions and governs the nonlinear dependence of water activity on water mole fraction (equation 3). The condensed phosphoric acids dissociate similarly and are assumed to interact with the water molecules analogously. Therefore, the functional dependence of the acid mixture solvent mole fraction  $\chi_1'$  is specified by equation 3 in this study.

Figure 3 graphically illustrates the dependency of solution water activity  $a_1$  on mole ratio of  $H_3PO_4$  (before association) to water for various degrees of acid association. The degree of association increases with the association parameter  $a$ , so that  $a = 1$  is a noncondensed pure  $H_3PO_4$  solution and  $a = 4$  is a highly condensed tetra-metaphosphoric acid solution. It is clear that, for the same mass of acid, the associated solution is characterized by a greater water activity and necessarily water vapor pressure. This indicates that, when the primary  $H_3PO_4$  molecules are partially associated, the vapor pressure lowering effect is diminished. As a result, the water vapor pressure gradients between solution droplet and environment are less severe for the condensed phosphoric acid solutions, an indication of reduced hygroscopicity.

In summary, the associated thermodynamic solution properties are established from the unassociated thermodynamics through molecule association and by neglecting the chemical differences between the original species and the associated species.

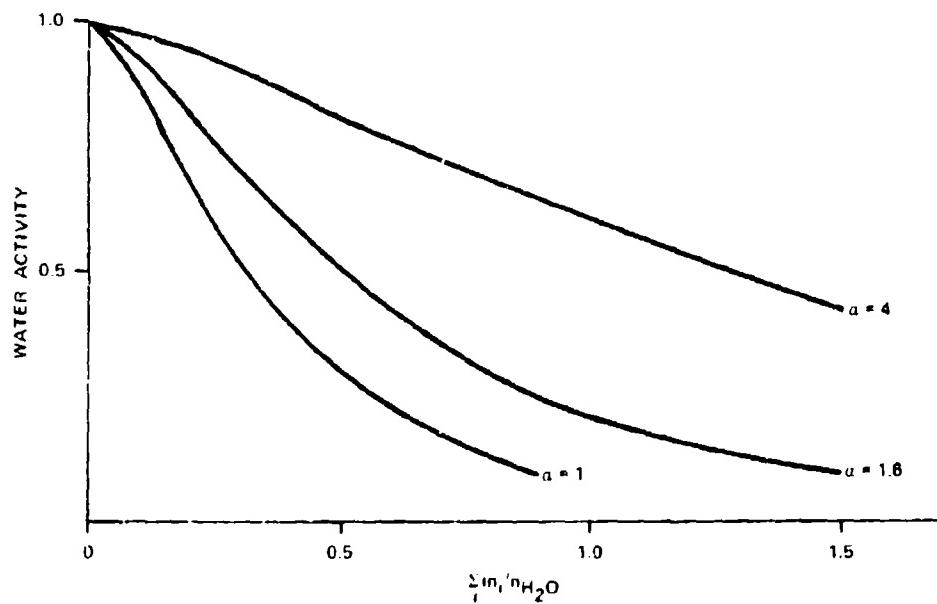


Figure 3. Water Activity of Various Condensed Phosphoric Acid Solutions as a Function of  $H_3PO_4$  Association

3.2

Equivalent  $H_3PO_4$  Phosphorus Smoke Acid Concentration.

By definition, the acid concentration of a multicomponent acid mixture is given as

$$F = \frac{\sum_{i=1}^m M_{i+2,1,31+1}^{n_i}}{\sum_{i=1}^m M_{i+2,1,31+1}^{n_i} + M_{H_2O}} \quad (13)$$

where  $M_{i+2,1,31+1}$  is the molecular weight of the  $i$ th order condensed phosphoric acid;  $i = 1$ , being  $H_3PO_4$ , is represented by  $M_{314}$ .

In this section, the equivalent  $H_3PO_4$  concentration is formulated in order to compare experiment and theory. The equivalent ortho acid concentration function assumes that each mole of NaOH dissolved in the acid solution can be equated to one  $H_3PO_4$  molecule as is customary in titration analysis.

For the case of the condensed phosphoric acids, the  $i$ th order condensed phosphoric acid will possess  $i$  titration end points.<sup>7</sup> Therefore, the total number of NaOH molecules dissolved in the condensed phosphoric acid solution is

$$[NaOH] = \sum_{i=1}^m n_i \quad (14)$$

Since each molecule of NaOH is equated with a compound having a molecular weight of  $H_3PO_4$ , the equivalent  $H_3PO_4$  mass is

$$\sum_{i=1}^m M_{i+2,1,31+1}^{n_i} = M_{314} \sum_{i=1}^m n_i \quad (15)$$

Substitution of equation 15 into equation 13 results in the equivalent  $H_3PO_4$  concentration of an arbitrary mixture of condensed phosphoric acids as

$$F_e = \frac{a M_{314} (1-x)}{M_{H_2O} x + a M_{314} (1-x)} \quad (16)$$

where  $x$  is given by equation 4. Figure 4 shows the dependence of equivalent  $H_3PO_4$  concentration on relative humidity for various condensed phosphoric acid solutions. As the solution becomes more condensed,  $F_e$  increases at constant relative humidity. This is an outgrowth of the reduced water absorbing characteristics of the condensed phosphoric acids. When the association parameter  $a$  is equal to unity (pure  $H_3PO_4$ ),  $F_e$  reduces to equation 6 as expected.

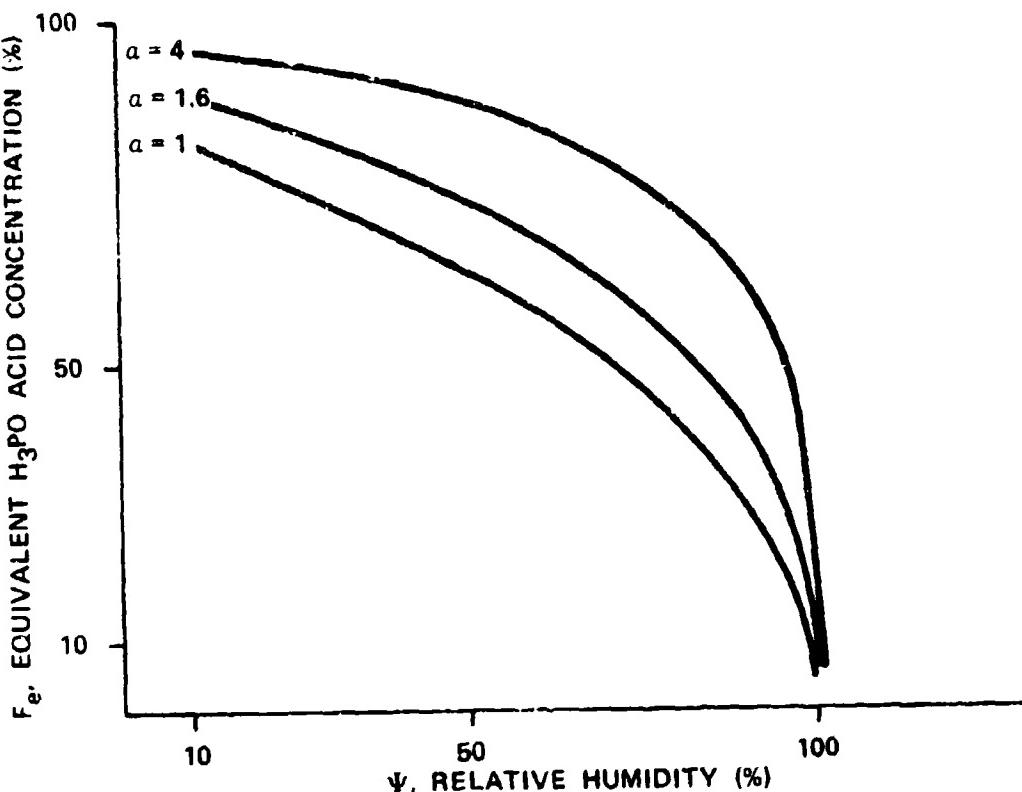


Figure 4. Equivalent  $\text{H}_3\text{PO}_4$  Acid Concentration of a Phosphorus Smoke Versus Degree of Acid Association

Now, for the present case, the mole ratio of pyrophosphoric acid to  $\text{H}_3\text{PO}_4$  is expressed in terms of the weight percentages as

$$\frac{n_2}{n_1} = \frac{w_{427}}{w_{314}} = \frac{M_{314}}{M_{427}} \cdot \frac{w_{427}}{w_{314}} \quad (17)$$

where  $w_{427}$  and  $w_{314}$  are the weight percentages of pyro and ortho, respectively. In putting the weight percentages experimentally measured by Kapishev,<sup>3</sup> the mole ratio is

$$\frac{n_{427}}{n_{314}} = 1.65 \quad (18)$$

Now each pyrophosphoric acid molecule converts to two  $\text{H}_3\text{PO}_4$  molecules through branch point hydration.<sup>5</sup> The corresponding mole ratio of acid mixture solute number  $\sum n_1$  to pure  $\text{H}_3\text{PO}_4$  solute number is

$$\frac{\sum n_1}{n_1} = 1.62 \quad (19)$$

But this is exactly the association parameter  $a$  defining the reduction in solute number due to the association of  $H_3PO_4$  molecules. Substitution of this value of  $a$  into equation 16 produces the equivalent  $H_3PO_4$  acid concentration of a phosphorus smoke. Figure 1 shows the good agreement between the experimental values of Anderson and those predicted by the mixture model over the relative humidity range from 25% to 90%.

### 3.3 Real Phosphorus Smoke Acid Concentration.

The equivalent  $H_3PO_4$  acid concentration function  $F_e$  misrepresents the real acid mixture concentration  $F_r$ . Although the equivalent acid concentration does account for the reduction in solute hygroscopicity through solute number reduction in the case of theoretical treatment and by measuring the reduced amount of water absorbed in the case of experiment, both treatments fail in describing the real acid concentration by imposing a one to one correspondence between  $NaOH$  and  $H_3PO_4$ . If one inspects the pyrophosphoric acid molecule  $H_4P_2O_7$ , then it is clear that two  $NaOH$  molecules are associated with a mass which is less than two  $H_3PO_4$  molecules. Specifically, the pyrophosphoric acid molecule is represented by  $2(H_3PO_4)-H_2O$ . The result is that the equivalent acid concentration function  $F_e$  overestimates the real mass of acid in the phosphorus smoke. More mathematically

$$\sum_{i=2}^M i^{n_i} < M_{314} \sum_{i=1}^n i^{n_i} \quad (20)$$

The real acid concentration function may be expressed in terms of the equivalent ortho acid concentration function by accounting for the molecular weight differences between multiples of  $H_3PO_4$  molecules and pH equivalent condensed phosphoric acids.

Beginning with the equivalent acid concentration  $F_e$

$$F_e = M_{314} \sum_{i=1}^n i^{n_i} / M_T \quad (21)$$

and the real acid concentration function  $F_r$

$$F_r = \sum_{i=2}^M i^{n_i} / M_T \quad (22)$$

the ratio of the two functions can be expressed as

$$\frac{F_r}{F_e} = \frac{\sum_{i=2}^M i^{n_i}}{M_{314} \sum_{i=1}^n i^{n_i}} \quad (23)$$

The sum in the numerator of equation 23 may be rewritten from equation 9 as

$$\sum_{i=1+2, i, 3i+1}^n = (M_{314} - M_{H_2O}) \cdot \sum_i n_i + M_{H_2O} \sum_i n_i \quad (24)$$

Combining equations 23 and 12 results in

$$\frac{F_r}{F_e} = \frac{M_{113} \sum_i n_i + M_{H_2O} \sum_i n_i}{M_{314} \sum_i n_i} \quad (25)$$

Finally substitution of equation 11 into equation 25 gives the defining relationship between  $F_r$  and  $F_e$  as

$$F_r = F_e \cdot \frac{M_{113} + M_{H_2O}/a}{M_{314}} \quad (26)$$

For any associated solution ( $a > 1$ ), the fraction is less than unity and the equivalent acid concentration exceeds the real acid concentration. Figure 5 depicts the percent deviation between  $F_e$  and  $F_r$  for a series of condensed phosphoric acid solutions. The deviations increase monotonically with the association parameter  $a$ , varying from zero at  $a = 1$  to  $-16\%$  at  $a = 4$ . Consequently, the greater the degree of acid association the greater the misrepresentation of the real acid concentration.

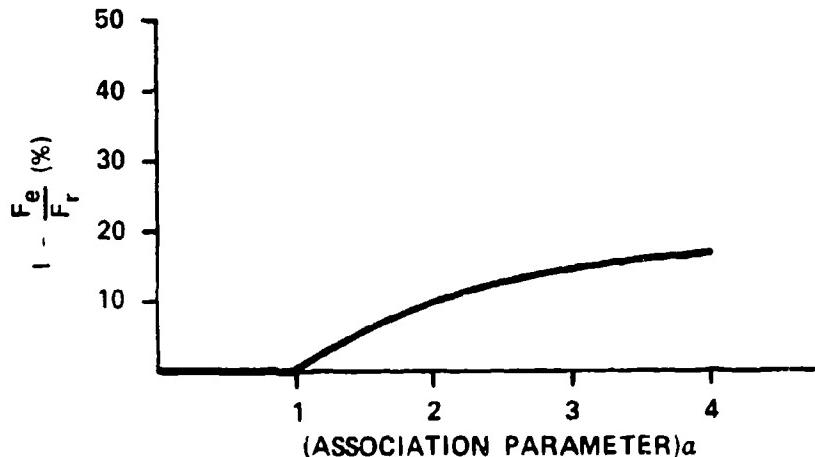


Figure 5. Percent Deviation between Equivalent  $H_3PO_4$  and Real Acid Concentration as a Function of Acid Association

For the present case,  $a = 1.62$  and

$$F_r = 0.93 F_e \quad (27)$$

Consequently, procedures involving titrations against standard 0.01 N NaOH solutions will overestimate droplet acid concentrations by as much as 7% when a one to one correspondence between moles of NaOH and  $H_3PO_4$  is assumed.

### 3.4 Yield Factor of a Phosphorus Smoke.

Following logic similar to the derivation of the  $H_3PO_4$  smoke (equation 7), the yield factor of a multicomponent acid smoke is given by

$$y.f. = \frac{\sum_{i=1}^M n_i}{M_p \cdot F_r} \quad (28)$$

Here the phosphorus aerosolization parameter  $\zeta$  and the composition parameter  $n$  are set to unity. Substituting for  $F_r$  from equation 23, the yield factor may be expressed as

$$y.f. = \frac{M_{314} \cdot \sum n_i}{M_p \cdot F_e} \quad (29)$$

Since  $i$  phosphorus atoms are tied up in the  $i$ th condensed phosphoric acid, then

$$M_p = M(P) \sum n_i \quad (30)$$

where  $M(P)$  is the mass of a phosphorus atom. The yield factor of a multicomponent phosphorus smoke becomes

$$y.f. = M_{314}/M(P) \cdot F_e \quad (31)$$

Comparison of equation 31 with the experimental yield factors of Tarnove<sup>6</sup> indicates good agreement over the range of relative humidities from 40% to 70%.

In conclusion, it has been demonstrated that the equilibrium properties of a phosphorus smoke cannot be predicted from a thermodynamic model which is based on the water activity of  $H_3PO_4$  solution. Based on high temperature  $P_4O_{10}$  studies, chemical composition of phosphorus smoke droplets is proposed to be a mixture of orthophosphoric and pyrophosphoric acid. Applying a solute number reduction scheme, the solution thermodynamics of the condensed phosphoric acids is formulated from the ortho water activity data. Comparison of mixture model synthetic data and experimental data indicates good agreement.

#### 4. CONCLUSIONS

4.1 A thermodynamic model which is based on the water activity of  $H_3PO_4$  solutions will underestimate phosphorus smoke acid concentrations by as much as 25% for relative humidities less than 90%. Furthermore, phosphorus smoke yield factors are overestimated by as much as 25% for relative humidities less than 90%.

4.2 Based on a solute number reduction scheme, the water activity of an arbitrary mixture of condensed phosphoric acids is formulated from existing  $H_3PO_4$  water activity data.

4.3 High temperature  $P_4O_{10}$  hydration studies suggest the chemical composition of phosphorus smoke droplets is a mixture of  $H_3PO_4$  and pyrophosphoric acid, whereupon the solution thermodynamics of the acid droplets is developed.

4.4 Comparison of mixture model synthetic data and experimental data indicates the condensed acid model predicts the acid concentrations and yield factors of a phosphorus smoke within 5%.

4.5 Due to the molecular weight differences between the condensed phosphoric acids and the pH equivalent multiple of  $H_3PO_4$  molecules, equivalent  $H_3PO_4$  concentrations will overestimate the acid concentrations of a phosphorus smoke by 7%.

#### LITERATURE CITED

1. Rubel, G. O. ARCSL-TR-78057. Predicting the Droplet Size and Yield Factors of a Phosphorus Smoke as a Function of Droplet Composition and Ambient Relative Humidity Under Tactical Conditions. November 1978.
2. Milham, M. E., Anderson, D. H., Fricke, R. H., and Tarnove, T. L. ARCSL-TR-77067. New Findings on the Nature of WP/RP Smokes. July 1977.
3. Kapishev, T. A., Bekturov, A. B., Kalmykov, S. I., and Nurseitov, Sh. Sh. Research In The Reaction Between Phosphorus Pentoxide And Water Vapors Izv. Akad. Nauk. Kaz. SSR, Ser. Khim. 28, No. 3 (1978).
4. Gillespie, G. R., and Johnstone, H. F. Particle Size Distribution in Some Hygroscopic Aerosols. Chem. Eng. Prog. 51, No. 2 (February 1955).
5. Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. VIII. Supplement III: Phosphorus. Wiley-Interscience, New York, New York. 1971.
6. Tarnove, T. L. ARCSL-TR-80049. Studies of the Chemistry of the Formation of Phosphorus-Derived Smokes and Their Implications for Phosphorus Smoke Munitions. October 1980.
7. Van Wazer, J. R. Phosphorus and Its Compounds. Vol I. Interscience Publishers, Inc., New York, New York. 1958.
8. Glasstone, S. Textbook of Physical Chemistry. 2d Ed. pp 676-678 1940.
9. Ogsten, A. G., and Winzer, D. J. J. Phys. Chem. 79, No. 23, 2497 (1975).

## GLOSSARY

a	association parameter
$a_1$	water activity
d	droplet diameter
F	orthophosphoric acid concentration
$F_e$	equivalent ortho acid concentration
$F_r$	real acid concentration
i	order of acid association
$M(H_3PO_4)$	molecular weight of orthophosphoric acid
$M(P)$	molecular weight of phosphorus
$M_p$	mass of phosphorus in starting material
$M_{H_2O}$	molecular weight of water
$M_t$	total droplet mass
$m_{H_2O}$	mass of water in droplet
$n_{H_2O}$	moles of water in droplet
$n_i$	moles of the i <sup>th</sup> order condensed phosphoric acid
P	pressure
S	droplet saturation ratio
T	temperature
$v_1$	molecular volume of water
$\sigma$	surface tension
$\zeta$	phosphorus aerosolization parameter
$\Psi$	relative humidity
$x_1$	water mole fraction

DISTRIBUTION LIST 5

Names	Copies	Names	Copies
<b>CHEMICAL SYSTEMS LABORATORY</b>			
ATTN: DRDAR-CLF	1	Deputy Chief of Staff for Research, Development & Acquisition	
ATTN: DRDAR-CLJ-R	3	ATTN: DAMA-CSS-C	1
ATTN: DRDAR-CLJ-L	3	ATTN: DAMA-ARZ-G	1
ATTN: DRDAR-CLJ-M	1	Washington, DC	
ATTN: DRDAR-CLJ-P	1	US Army Research and Development Command Group (Europe)	
ATTN: DRDAR-CLT-E	1	ATTN: DRXSN-E-SC	
ATTN: DRDAR-QLN	2	LTC J.M. Dorrance	
ATTN: DRDAR-CLW-C	1	Box 65, FPO New York 09510	1
ATTN: DRDAR-CLB-C	1	HQDA (DAMI-FIT)	
ATTN: DRDAR-CLB-P	1	WASH, DC 20310	
ATTN: DRDAR-CLB-PA	1	Commander	
ATTN: DRDAR-CLB-R	1	DARCOM, STITEUR	
ATTN: DRDAR-CLB-T	1	ATTN: DRXST-STI	
ATTN: DRDAR-CLB-TE	1	Box 48, APO New York 09710	1
ATTN: DRDAR-CLY-A	1	Commander	
ATTN: DRDAR-CLY-R	6	US Army Science & Technology Center- Far East Office	
ATTN: DRDAR-CLR-I	1	ATTN: MAJ Borges	
COPIES FOR AUTHOR(S):			
Research Div	1	APO San Francisco 96328	
<b>DEPARTMENT OF DEFENSE</b>			
Defense Technical Information Center			
ATTN: DTIC-CDA-2	12	Commander	
Cameron Station, Building 5		2d Infantry Division	
Alexandria, VA 22314		ATTN: EAIDCOM	
		APO San Francisco 96224	1
Director		Commander	
Defense Intelligence Agency		5th Infantry Division (Mech)	
ATTN: DB-4G1	1	ATTN: Division Chemical Officer	
Washington, DC 20301		Fort Polk, LA 71459	1
Special Agent In Charge		OFFICE OF THE SURGEON GENERAL	
ARO, 902d Military Intelligence GP		Headquarters	
ATTN: IAGPA-A-AN		US Army Medical Research and Development Command	
Aberdeen Proving Ground, MD 21005		ATTN: SGRD-PL	
		Fort Detrick, MD 21701	1
Commander		Commander	
SED, HQ, INSCOM		USA Biomedical Laboratory	
ATTN: IRFM-SED (Mr. Joubert)	1	ATTN: SGRD-UV-L	
Fort Meade, MD 20755		Aberdeen Proving Ground, MD 21010	1
<b>DEPARTMENT OF THE ARMY</b>			
IQDA (DAMO-NCC)	1		
WASH DC 20310			

US ARMY HEALTH SERVICE COMMAND

Superintendent  
Academy of Health Sciences  
US Army  
ATTN: HSA-CDH  
ATTN: HSA-IFM  
Fort Sam Houston, TX 78234

US ARMY MATERIEL DEVELOPMENT AND  
READINESS COMMAND

**Commander**  
**U.S. Army Materiel Development and**  
**Readiness Command**  
**ATTN: DRUDC**  
**ATTN: DRUSF-R**  
**5001 Eisenhower Ave**  
**Alexandria, VA 22333**

Commander  
US Army Foreign Science & Technology  
Center  
ATIN: DDXST-MT3  
220 Seventh St., NE  
Charlottesville, VA 22901

Director  
US Army Materiel Systems Analysis  
Activity  
ATTN: DRXSY-MP  
ATTN: DRXSY-T (Mr. Metz)  
Aberdeen Proving Ground, MD 21005

Commander  
US Army Missile Command  
Redstone Scientific Information  
Center  
ATTN: CRSMI-RPR (Documents)  
Redstone Arsenal, AL 35809

Director  
DARCOM Field Safety Activity  
ATTN. DRXDS-6  
Watertown, LS 47111

### **Commander**

US Army Natick Research &  
Development Command  
ATTN: DRDNA-VR  
ATTN: DRDNA-VT  
Natick, MA 01760

US ARMY ARMAMENT RESEARCH AND  
DEVELOPMENT COMMAND

Commander  
US Army Armament Research and Development Command

ATTN: DRDAR-LCA-L 1  
ATTN: DRDAR-LCE 1  
ATTN: DRDAR-LCE-C 1  
ATTN: DRDAR-LCU 1  
ATTN: DRDAR-LCU-CE 1  
ATTN: DRDAR-PMA (S.R. Sacco) 1  
ATTN: DRDAR-SCA-W 1  
ATTN: DRDAR-TSS 2  
ATTN: DRCPM-CAWS-AM 1  
ATTN: DRCPM-CAWS-SI 1  
Cover: NJ 07801

Director  
Ballistic Research Laboratory  
ARADCOM  
ATTN: DRDAR-TSB-S  
Aberdeen Proving Ground, MD 21005

US ARMY ARMAMENT MATERIEL READINESS  
COMMAND

Commander  
US Army Armament Materiel  
Readiness Command  
ATTN: DRSAR-ASN  
ATTN: DRSAR-PDM  
ATTN: DRSAR-SF  
Fort Island, HI 61298

1 Commander  
US Army Dugway Proving Ground  
ATTN: Technical Library  
Docu Sect  
Dugway, UT 84022

1 US ARMY TRAINING & DOCTRINE COMMAND

Commandant  
U.S. Army Infantry School  
ATTN: NBC Division  
Fort Benning, GA 31905

Commandant USAMP&CS/TC&FM ATTN: ATZN-CM-ODM Fort McClellan, AL 36205	1	Commander Naval Weapons Center ATTN: Technical Library Code 343 China Lake, CA 93555	1
Commander US Army Infantry Center ATTN: ATSI-CD-MS-C Fort Benning, GA 31905	1	Commander Officer Naval Weapons Support Center ATTN: Code 5042 Dr. B.E. Doude Orane, IN 47522	1
Commander US Army Infantry Center Directorate of Plans & Training ATTN: AT2B-DPT-PO-NBC Fort Benning, GA 31905	1	US MARINE CORPS	
Commander USA Training and Doctrine Command ATTN: ATCD-Z Fort Monroe, VA 23651	1	Director, Development Center Marine Corps Development and Education Command ATTN: Fire Power Division Quantico, VA 22134	1
Commander USA Combined Arms Center and Fort Leavenworth ATTN: ATZL-CA-COG ATTN: ATZL-CAM-IM Fort Leavenworth, KS 66027	1	DEPARTMENT OF THE AIR FORCE	
Commander US Army TRADOC System Analysis Activity ATTN: ATAA-SL White Sands Missile Range, NM 88002	1	HQ Foreign Technology Division (AFSC) ATTN: TQTR Wright-Patterson AFB, OH 45433	1
US ARMY TEST & EVALUATION COMMAND		HQ AFLC/LOWMM Wright-Patterson AFB, OH 45433	1
Commander US Army Test & Evaluation Command ATTN: DRSTE-CM-F ATTN: DRSTE-CT-T Aberdeen Proving Ground, MD 21005	1	OUTSIDE AGENCIES	
DEPARTMENT OF THE NAVY		Battelle, Columbus Laboratories ATTN: TACTEC 505 King Avenue Columbus, OH 43201	1
Commander Naval Explosive Ordnance Disposal Facility ATTN: Army Chemical Officer Code AC-3 Indian Head, MD 20540	1	Toxicology Information Center, WG 1008 National Research Council 2101 Constitution Ave., NW Washington, DC 20418	1